

FLUORITE'S PRECIPITATION IN KOH SOLUTIONS IN VIEW OF REMOVING FLUORIDES FROM WASTEWATERS

R. Tavares^a, D. Garcia^a, J. Moutte^a, A. Cameirao^a, G. Fevotte^{a,b}, D. Amaraggi^c,
B. Morel^c

^aENSMSE, Centre SPIN, 158 cours Fauriel, 42023 Saint-Etienne, France

^b Université Lyon 1, 43 bd du 11 Novembre 1918, 69100 Villeurbanne, France

^cAREVA-COMURHEX, Zone Industrielle du Tricastin, 26701 Pierrelatte, France

Keywords: fluorite, portlandite, carbonate, KOH solution, Pitzer model, solubility

The process under study aims at removing dissolved fluorides from effluent waters through the addition of calcium and the precipitation of fluorite in a fluidized bed. In the concept developed at COMURHEX, the effluent is a highly concentrated KOH solution and the calcium is provided as a suspension of portlandite with calcite as an impurity. COMURHEX's target is to achieve an efficient defluorination of KOH solutions prior to recycling and to control the growth of the fluorite grains. Since building a fluorite crystallisation model requires a thermodynamic basis, we started exploring portlandite, calcite and fluorite solubility in concentrated KOH solutions.

We are primarily concerned with equilibria in the system $\text{Ca}(\text{OH})_2\text{-CaCO}_3\text{-CaF}_2\text{-KOH-H}_2\text{O}$ at temperatures 15 – 35°C in KOH solutions up to 6M (340g/kg). Suspensions and mixtures are prepared in a 3 L stirred reactor under N_2 atmosphere and the temperature is varied. Liquid samples are taken from the reactor, filtered, diluted, and analysed by ICP-AES for cations and ionic chromatography for anions, while the solids are washed in ethanol and observed by SEM.

In order to choose materials and improve techniques, this work was started with the $\text{Ca}(\text{OH})_2\text{-CaCO}_3\text{-KOH-H}_2\text{O}$ subsystem, where solubility data and speciation models are already available from the literature [1]. In this subsystem we experienced the analytical and kinetic difficulties already quoted by other authors [2].

Albeit ICP-AES is very sensitive, Ca analysis is difficult in KOH solutions, because portlandite solubility is low and a matrix effect of potassium weakens the Ca signal, so that its calibration must be performed using KOH solutions rather than conventional (dilute) standards. This problem was overcome by using the standard addition method where the calibrating solutions are prepared at the same KOH concentration as the unknown samples and spiked with increasing amounts of calcium. This method enables the absolute calcium variations to be calibrated and the calcium present as impurities in the KOH parent solution (and thus in the standards) to be evaluated by regression.

According to [1], the carbonate solute content increases strongly with increasing KOH concentrations at equilibrium with calcite. Despite its enhanced solubility, however,

calcite reacts slowly in KOH solutions to produce secondary portlandite, and although equilibrium with portlandite seems to be obtained quickly, much of our runs remained undersaturated with respect to solid carbonate.

Despite these difficulties, our values of calcium hydroxide solubility compare well with those found in the literature [2] and extend the range of KOH concentrations and the temperatures where these data can be used to constrain thermodynamic models.

We used the ARXIM code, developed at Ecole des Mines de Saint Etienne, to compare these experimental solubility data with aqueous speciation models (figure 1).

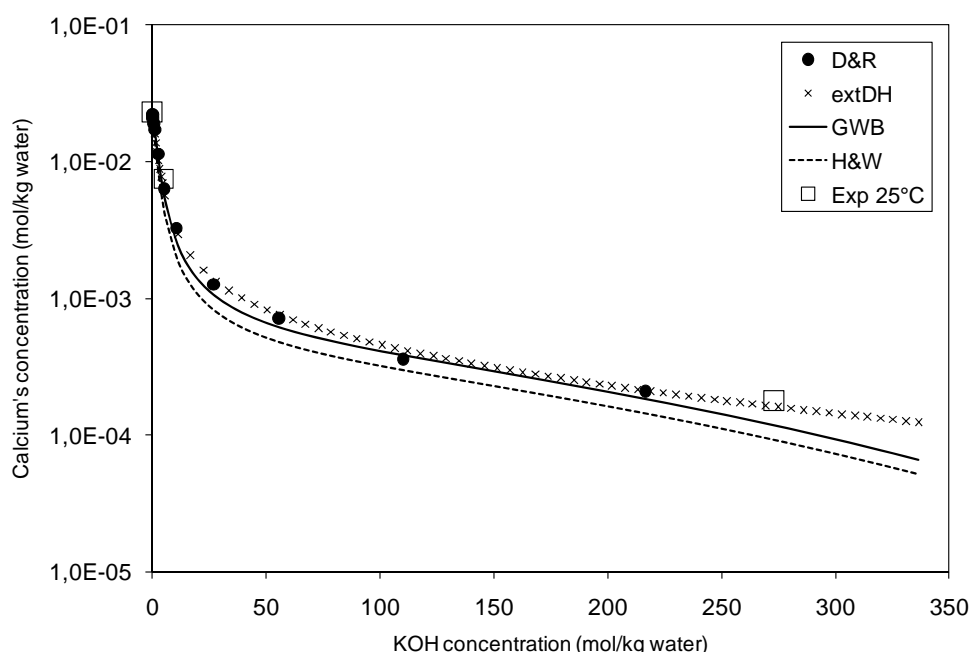


Figure 1. Calcium contents at equilibrium with portlandite in KOH solutions as predicted by extended Debye-Huckel (b-dot) model and various types of Pitzer's model parametrizations (GWB, H&W) at 25°C. Model equilibrium curves are compared with values obtained in the experiments (Exp 25°C) and those obtained by [2] (D&R).

Our experimental solubility values and those referenced in [1] for calcium compare well with those calculated with an extended Debye-Huckel (b-dot) and Pitzer type models. Quite unexpectedly, the extended Debye-Huckel model fits very well experimental data for calcium up to very high KOH concentrations. However, Pitzer-type models account much better for the carbonate enrichment in solutions equilibrated with both calcite and portlandite at high KOH concentrations.

To constrain the conditions of fluorite precipitation in the process, we need now to extend the speciation model to the system $\text{Ca}(\text{OH})_2\text{-CaCO}_3\text{-CaF}_2\text{-KOH-H}_2\text{O}$. Since a Pitzer model describes better the system's behaviour, we need to determine new Pitzer's interaction parameters in the range 15-35°C. Many of the required parameters are already documented at 25°C [2, 3, 4, 5], but fewer interaction data are documented as a function of temperature [6, 7, 8, 9, 10]. Thus, experiments are needed in order to

determine the parameters for the interactions $\text{Ca}^{2+}/\text{F}^-$, $\text{Ca}^{2+}/\text{CO}_3^{2-}$ and for $\text{F}^-\text{-OH}^-$. As first approximation we will consider that parameters for triple and ionic interactions of the same sign are negligible.

Mineral equilibria in this system will be explored by mixing KOH-KF solutions with suspensions of portlandite and/or calcite in KOH solutions. The guess is to locate the four phase equilibrium point (portlandite-calcite-fluorite-solution) as a function of KOH concentration and temperature. Of particular interest is the location of the portlandite-absent univariant line, which may exert a major control on process solutions (figure 2).

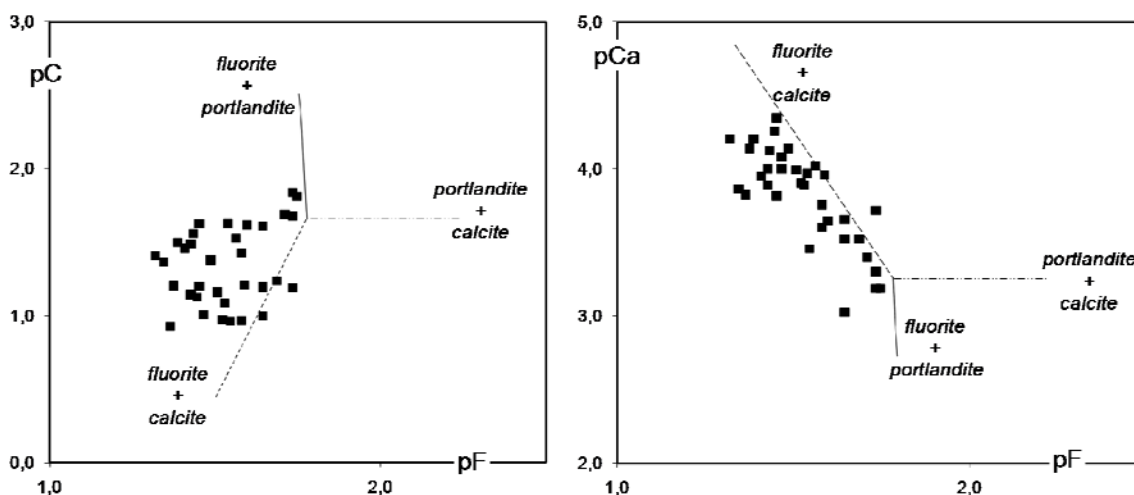


Figure 2. Hypothetical phase relationships for the system portlandite-calcite-fluorite in KOH solutions of fixed concentration. Solution compositions for Ca, F and C are reported as P-values ($P = -\log C$) at equilibrium with solids and compared with test process data (squares).

Possible scenarios for fluorite precipitation and their kinetic limitations will ultimately rely on the assessment of over and undersaturations of the process solutions with respect to the three minerals.

References:

- [1] Reardon, E., Fagan, R. The calcite/portlandite phase boundary: enhanced calcite solubility at high pH. *Applied Geochemistry* **2000**, 15, 327-335
- [2] Duchesne, J., Reardon, E., Measurement and prediction of portlandite solubility in alkali solutions, *Cem. Concr. Res.* **1995**, 25, 1043-1053
- [3] Christov, C., Møller, N. A chemical equilibrium model of solution behaviour and solubility in the H-Na-K-Ca-OH-Cl-H₂SO₄-SO₄-H₂O system to high concentration and temperature, *Geochimica & Cosmochimica Acta* **2004**, vol 68, 18, 3717-3739
- [4] Harvie, C., Møller, N., Weare, J. The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system to ionic strengths at 25°C, *Geochimica & Cosmochimica Acta* **1984**, 48, 723-751

- [5] Pitzer, K., Mayorga, G. Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent, *The Journal of Physical Chemistry* **1973**, 19, 77, 2300-2308
- [6] Christov, C., Møller, N., A chemical equilibrium model of solution behavior and solubility in the H-Na-K-Ca-OH-Cl-HSO₄-SO₄-H₂O system to high concentration and temperature, *Geochimica & Cosmochimica Acta* **2004**, 18, 68, 3717-3739
- [7] Roy, R., Gibbons, J., Williams, R., Godwin, L., Baker, G., Simonson, J., Pitzer, K. The thermodynamics of aqueous carbonate solutions II. Mixtures of potassium carbonate, bicarbonate and chloride, *J. Chem. Thermodynamics* **1984**, 16, 303-315
- [8] Greenberg, J., Møller, N., The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Cl-SO₄-H₂O system from 0°C to 250°C, *Geochimica & Cosmochimica Acta* **1989**, 53, 2053-2518
- [9] Christov, C., Møller, N., Chemical equilibrium of solution behavior and solubility in the H-Na-K-OH-Cl-HSO₄-SO₄-H₂O system to high concentration and temperature, *Geochimica & Cosmochimica Acta* **2004**, 6, 68, 1309-1331
- [10] Ott, J., Boerio-Goates J., *Chemical thermodynamics: Principles and Applications*, Academic Press, **2000**.